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REACTIONS OF DISSOLVED POLLUTANTS WITH OZONE IN AQUEOUS SOLUTIONS

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ABSTRACT

This research was undertaken to investigate kinetics of liquid phase oxidation of selected hydrocarbons by ozone. Rate constants and orders of the ozonation reactions in aqueous solutions of pH values varying from 3 to 7 at 5 to 35°C were determined utilizing the stopped-flow technique.

Ozonation reactions of olefinic compounds including cyclohexene, cyclopentene and 1-pentene were much faster in aqueous solutions than in the vapor phase. The rate constants of the bimolecular reactions are of the order of 1×10^6 1/mole-sec. or larger, and are nearly independent of the pH value and temperature. Experimental results indicate that saturated hydrocarbons such as cyclohexane, cyclopentane, hexane and pentane were not reactive with dissolved ozone in solutions. Benzene and toluene reacted with ozone at moderate rates in acidic solutions, but the ozonation of benzene was very rapid in neutral solutions yielding a first order rate constant of 12.2 sec^{-1} at 25°C. Orders of the ozonation of aromatic compounds changed with acidity indicating a possible shift in mechanisms of the reactions.

Preliminary tests by the method of chromatography showed that acids and aldehydes were formed in ozonation of the olefins and that oxidation of benzene produced benzoquinone and hydroquinone. Polymerization of the hydrocarbons was indicated by detections of high molecular species in the solutions.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

ac	--alternating current
A/D	--analog to degital
°C	--degree centigrade
cm	--centimeter
dc	--direct current
GC	--gas chromatograph
K cal/g mole	--kilocalorie per gram mole
l	--liter
l/min	--liter per minute
l/mole-sec	--liter per mole per second
min.	--minute
ml	--milliliter
M	--molar or moles of solute per liter of solution
$M^{-1}cm^{-1}$	--per molar per centimeter
nm	--nanometer
pH	--logarithm of the reciprocal of hydrogen ion concentration in gram atoms per liter
pKa	--logarithm of the reciprocal of dissociation constant
psig	--pound per square inch at gauge pressure
sec	--second
sec^{-1}	--per second
v	--volt
µl	--microliter

SYMBOLS

A(t)	--absorption as a function of time
b	--length of light path
C_A	--concentration of ozone
C_{AO}	--initial concentration of ozone
C_B	--concentration of hydrocarbon
C_{BO}	--initial concentration of hydrocarbon
C_i	--concentration of component i
CCl_4	--carbon tetrachloride
CH_3COOH	--acetic acid
ΔE	--activation energy
f	--frequency factor
HCl	--hydrogen chloride
H_2O	--water
H_3PO_4	--phosphoric acid
I	--ionic strength
I_2	--iodine
k_1	--rate constant for decomposition reaction
k_2	--rate constant for ozonation reaction
k'	--apparent rate constant
KI	--potassium iodide
KOH	--potassium hydroxide
l	--order of decomposition reaction

m	--order with respect to ozone concentration in ozonation reaction
n	--order with respect to hydrocarbon concentration in ozonation reaction
NaH_2PO_4	--sodium dihydrogen phosphate
Na_2HPO_4	--disodium hydrogen phosphate
NaI	--sodium iodide
NaOH	--sodium hydroxide
$Na_2S_2O_3$	--sodium thiosulfate
$Na_2S_4O_6$	--sodium tetrathionate
O_2	--oxygen
O_3	--ozone
t	--reaction time
T	--absolute temperature
ε	--absorption coefficient
Z_i	--number of ion charges for component i

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SECTION 1

INTRODUCTION

Hydrocarbons are among the major pollutants (2,16) emitted into the atmosphere from mobile and stationary sources such as automobiles, petroleum refineries and chemical manufacturing facilities. Although atmospheric hydrocarbons vary considerably in structure, many species are reactive and may be oxidized to form secondary and tertiary pollutants. One of the most important oxidizing agents in the atmosphere is ozone produced in photochemical reactions in the troposphere and the stratosphere. Oxidation of the atmospheric hydrocarbons by ozone in vapor and liquid phases can result in productions of chemical species which are hazardous to public health and environment (14,16,17). Under overcast, high-humidity conditions, dissolved pollutants may be oxidized to secondary and tertiary aerosols in liquid phase though the rates and mechanisms of conversion are not well known (17,18). The present research, therefore, was undertaken to investigate kinetics of oxidation of some saturated hydrocarbons, olefins and aromatic compounds by ozone in aqueous phase. The compounds chosen for this study include benzene, cyclohexane, cyclohexene, cyclopentane, cyclopentene, hexane, pentane, 1-pentene and toluene.

Saturated hydrocarbons are not considered very reactive with ozone in vapor phase (16). Olefin-ozone reactions are very important in polluted atomspheres (2,14,16). The second order rate constants for vapor phase

ozonation of the selected olefins vary from about 3×10^3 to 4×10^4 1/mole-sec., and a variety of products can be formed (2,16). The reaction of ozone with benzene derivatives in the vapor phase has received little attention because of low reactivity (24). Mechanisms have been proposed for oxidation of many olefins and aromatic compounds by ozone in liquid phase (3,4,5,11,13,21). Rates of the oxidation have been reported for some reactions in organic solvents, but little information is available in the literature concerning the ozonation reactions in aqueous solutions (1,7,10,15,24, 25).

A stopped-flow spectrophotometer system was utilized in this research to study the kinetics of the proposed reactions. The apparatus is advantageous in measuring absorbance and, in turn, concentration changes during a rapid reaction by mixing of two liquid reactants with greater than 99.5% completion in 0.0005 to 0.002 seconds (9,12,13,23). A data acquisition system has been developed (8,9) utilizing hardware components made available by the Environmental Protection Agency, to collect, analyze and compile the kinetic data. Rate constants and orders of the ozonation were determined for the reactions in aqueous solutions of various pH values at different temperatures. By employing a gas chromatograph and a mass spectrometer, preliminary tests were conducted to detect products of the reactions in aqueous solutions.

SECTION 2

CONCLUSIONS

Rates of oxidation of selected hydrocarbons by ozone in acidic and neutral solutions were measured utilizing the stopped-flow technique. The kinetic experiments were conducted at temperatures varying from 5 to 35°C in solutions of a constant ionic strength of 0.1.

Saturated hydrocarbons including cyclohexane, cyclopentane, hexane and pentane studied in this research were not very reactive with ozone in aqueous phase. The three-halves order rate constants for these systems are about 0.13 $(mole/l)^{-1/2}$ sec^{-1} at 25°C in neutral solutions; this value is slightly larger than the rate constant for self decomposition of ozone without any contaminants in the solutions at similar conditions.

Cyclohexene can react rapidly with ozone in an aqueous solution at a half-life of less than one millisecond. The kinetics of ozonation was first order with respect to both concentrations of ozone and cyclohexene. The reaction yielding an average second order rate constant of 3.9×10^6 1/mole-sec. was influenced very little by the pH and temperature of the solutions. Although reliable information on very rapid kinetics of ozonation of cyclopentene and 1-pentene could not be obtained because of equipment limitations, the reaction rate constants are estimated to be of the order of 1×10^7 1/mole-sec.

The rate of ozonation of benzene was much faster than that of toluene in neutral solutions though the two systems proceeded at about the same moderate rates in acidic solutions. The first order ozonation rate constant

is 12.2 sec^{-1} for the benzene-ozone reaction at 25°C in neutral solutions. The rate of ozonation of benzene increased more significantly with temperature in acidic than in neutral solutions. The kinetics of ozonation was first order with respect to ozone but independent of benzene concentration in a neutral solution. However, the reaction was one-half order in both concentrations of benzene and ozone in acidic solutions. The ozonation reaction of toluene was first order with respect to concentration of ozone only in acidic solutions but the reaction was second order in neutral solutions with first order each in toluene and ozone concentrations. Results of preliminary tests seem to suggest that benzoquinone was formed in acidic solutions and that further reaction to hydroquinone was possible in neutral solutions.

The results of this research indicate that benzene, cyclopentene and cyclohexene can react with ozone much faster in aqueous solutions than in vapor phases. Liquid phase oxidation by ozone, therefore, can play a significant role in formation and removal of these and other organic aerosols in the atmosphere. The ozonation reactions tend to be bimolecular in nature as suggested by the stoichiometric ratios determined in this work. Mechanisms of the ozonation reactions may shift according to acidity causing changes in orders of reactions of the aromatic compounds.

SECTION 3

RECOMMENDATIONS

Experimental studies of oxidation of olefinic and aromatic compounds by ozone in aqueous solutions should be continued. Results of the present research for ozonation of selected hydrocarbons indicate that the oxidation reactions in aqueous phase can be many times faster than the reactions in vapor phase. Therefore, it is important to continue the experiments to determine the role of liquid phase reaction played by major pollutants in aerosol drops.

Investigations of mechanisms of liquid phase ozonation of selected hydrocarbons should be initiated. The kinetic measurements and preliminary product analyses obtained in this study tend to suggest that the mechanisms and products of reactions are sensitive to acidity of a solution. Results of the investigations can provide useful information regarding origin, fate and transport of secondary and tertiary aerosols in the atmosphere.

Rapid reactions between ozone and some hydrocarbons in aqueous solution demonstrate that mass transport and chemical reaction in liquid drops can be an important phenomenon controlling formation and growth of aerosol products. It is well known that the mass transfer of gaseous pollutants into liquid can be enhanced significantly by rapid chemical reactions. In addition to vapor phase reactions, therefore, it is desirable to take into account simultaneous absorption and oxidation of gaseous species by liquid drops in modeling of acid rains and other precipitations.

SECTION 4

MATERIALS AND EQUIPMENT

PRODUCTION OF OZONE GAS

Ozone gas was produced by passing a stream of extra dry oxygen through a Welsbach Model T-408 Laboratory ozonator (12,13). The ozonator is operated on the corona discharge principle. By imposing a high ac voltage across a discharge gap in the presence of an oxygen-containing gas, ozone is produced from the ozonator by the following reaction:

$$3O_2 \longrightarrow 2O_3 \qquad (1)$$

The efficiency is very low by this method, because only about 10% of the energy is utilized to produce ozone. The remainder is converted to light, sound and primary heat and, therefore, heat has to be removed by a water cooling system. Otherwise, a build-up of high temperature in the discharge space will reduce the yeild of ozone since decomposition of ozone is very temperature sensitive. The concentration of ozone produced by the ozonator is affected by several factors, including flow rate of the gas stream, voltage, gas pressure, impurity of the gas stream and temperature of the cooling system. A trace amount of water is not allowed in ozone producing chamber (12). Therefore, the use of extra dry oxygen of -60°F dew point is recommended. If the equipment is not used for more than 24 hours, it has to be purged with extra dry air or oxygen at least for 30 minutes before production of ozone.

The ozonator is operated on 115 volt, 50/60 cycles, single phase power supply. The oxygen gas pressure has to be regulated to 10-18 psig and

adjusted at 5-8 psig in the ozone producing chamber. The gas stream can be adjusted and measured at a flow rate between 0.5 to 2.0 l/min. The voltage can be set between 70 to 115 volts depending on the desired concentration of ozone. Tap water is used in the cooling system. To achieve a high concentration of ozone in the gas stream, a small flow rate, high voltage and pressure, and temperature of the cooling system should be applied.

The ozone outlet is first connected to an empty washing bottle then to a second washing bottle containing an appropriate buffer solutions. The remaining ozone is allowed to pass through a third empty washing bottle then absorbed in potassium iodide solution contained in a fourth bottle. The use of Tygon tubing, a good ozone resistant flexible material, is recommended for all connections in the output streams from the ozonator.

PREPARATION OF BUFFER AND AQUEOUS SOLUTIONS

Buffer solutions were prepared by adding appropriate amount of ACS grade chemicals such as HCl, NaH_2PO_4, Na_2HPO_4, H_3PO_4, or NaOH in distilled water for control of pH value and ionic strength. Any contaminants in the distilled water were oxidized by bubbling of ozone gas for at least 30 minutes and the residual ozone swept by nitrogen gas before preparing the buffer solutions.

Quantities of the various chemicals were determined from the following Henderson-Hasselbalch equation:

$$pH = pKa + \log \frac{[salt]}{[acid]} \qquad (2)$$

The ionic strength of a buffer solution is controlled by

$$I = 1/2 \sum_i C_i z_i^2 \qquad (3)$$

where C_i is the molal concentration of component i, and Z_i represents the number of charges of ion for component i.

In the present research, pH values of the solutions were controlled in

the range of 3 to 9 and the ionic strength was maintained at 0.1 in all solutions. The pH value of a solution was measured by a Sargent-Welch Model NX pH meter. All buffer solutions were utilized within 2 weeks after preparation.

Highest grade hydrocarbons available from various suppliers were purchased for this research. The suppliers and purities of the hydrocarbons are listed in Table 1. For each compound, a stock solution of a certain concentration was first prepared by dissolving appropriate amounts in 1000 ml of buffer solution of desired pH value, and the mixed solutions stirred for 5 to 40 hours to achieve homogeneity. The stock solution was then diluted using buffer solutions of the same pH value to obtain reactant solutions with concentrations varying from 1.0×10^{-3} to 1.0×10^{-5}M. The solutions were kept in a cool and dark place, and used within a few days to avoid degradation.

STOPPED-FLOW SPECTROPHOTOMETER SYSTEM

The apparatus used in the kinetic experiments is a Durrum-Gibson Model D-110, stopped-flow spectrophotometer. It is a complete system for rapid mixing of two liquid reactants and for measurement of the change in optical absorbance as a function of time at a wavelength ranging from 200 to 800 nm. This system consists of six functional subsystems as shown in Figure 1. The subsystems are described below:

(1) The sample flow subsystem - includes reservoir syringes, drive syringes, valve blocks, sample mixing jet, observation cuvette and stop syringes.

(2) The flow actuating subsystem - initiates the sample flowing for each reaction run. The flow rate obtained from this system is 10 m/sec. A filtered air or nitrogen supply regulated at 70 psig is required.

(3) The optical subsystem - supplies monochromatic light by means of a

TABLE 1. PURITIES AND SUPPLIERS OF HYDROCARBONS

Hydrocarbon	Supplier	Lot Number	Purity
Benzene	Aldrich Chemical Co.	EE4903TD	99+%, thiophene free
Cyclohexane	Aldrich Chemical Co.	EH98-6CE	99+%
Cyclohexene	Phillips Petroleum Co.	Z-996	99+%
Cyclopentene	J.T. Baker Chemical Co.	602001	99+%
Cyclopentene	Aldrich Chemical Co.	PD042687	99%
Hexane	Fisher Scientific Co.	780323	99+%
Pentane	Eastman Kodak Co.	D7C	98+%
Toluene	Aldrich Chemical Co.	LC072187	99+%

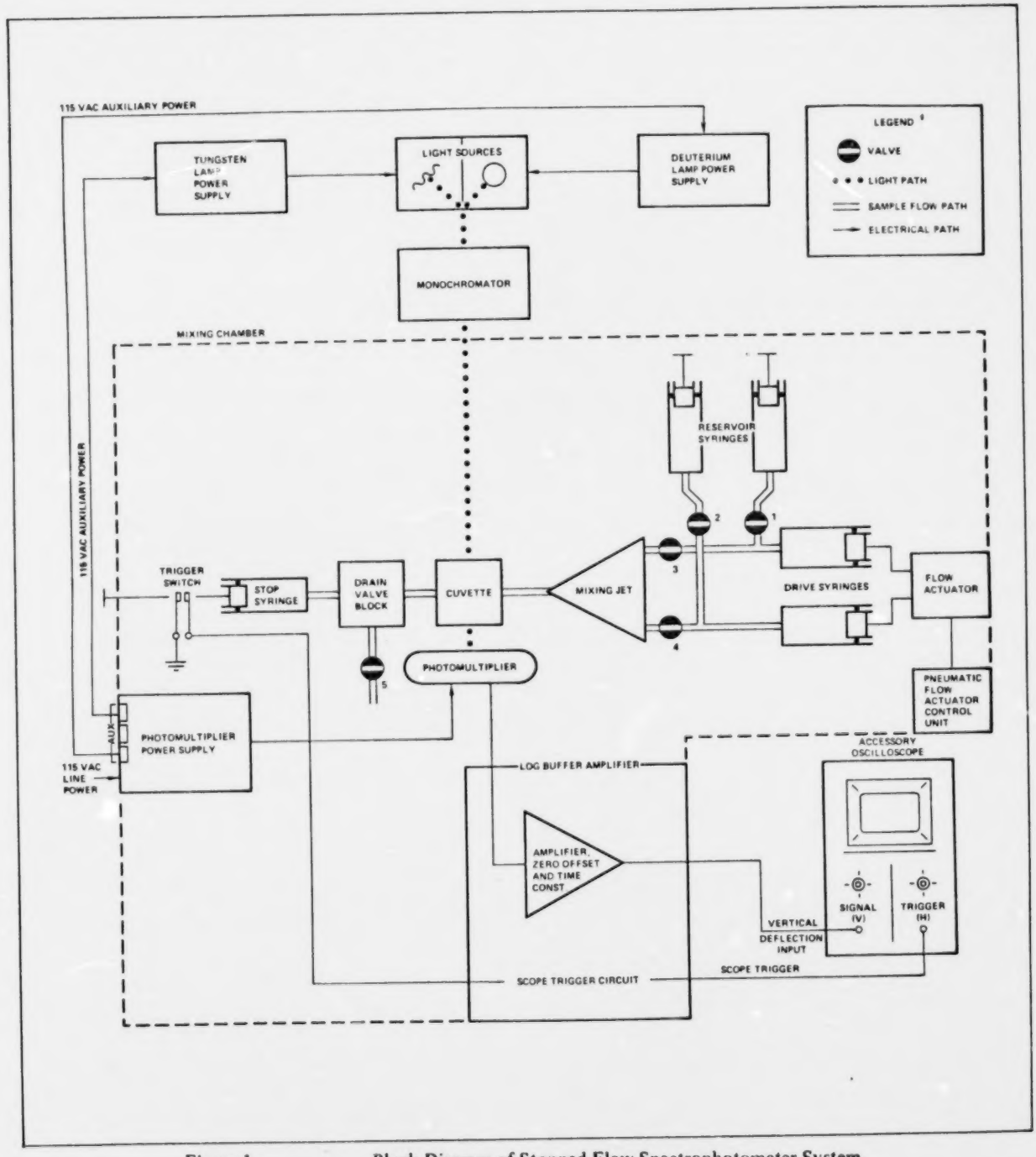


Figure 1 **Block Diagram of Stopped-Flow Spectrophotometer System.**

light source and monochromator and routes it through the cuvette and into the photomultiplier tube.

(4) The electronics - provide power for all electrically operated components and calibrated readout/display processing for the measurement signal from the photomultiplier. The log buffer amplifier serves an important function for the signal display on the oscilloscope or input to the data acquisition system. A large time constant setting provides a stable signal but a slow response. On the other hand, a fast response but unstable signal can be obtained by using a small time constant.

(5) The temperature control subsystem - circulates a coolant (eg. water) that maintains a constant temperature for all the parts of the flow subsystem. In the present research, a constant temperature bath, a Forma Scientific Model 2067 circulating system was used to maintain the circulating liquid at a desired temperature.

(6) Data recording devices - A Hewlett Packard 1207 A storage oscilloscope, a Model 198 A oscilloscope camera and a Model 680 strip chart recorder.

The kinetic experiments were conducted under isothermal conditions by fluid (usually, water) circulation through the stopped-flow spectrophotometer system to maintain a desired temperature. The stopped-flow equipment can be operated following appropriate valve settings and filling of two reactants in the drive syringes from the two separate reservoir syringes. Then, the valves may be reset for measurement of absorbance during a reaction. By activating the flow acturator, two solutions containing a hydrocarbon and dissolved ozone in the two separate drive syringe can be forced to mix rapidly (99.5% complete within 0.0005 to 0.002 sec.) in the mixing jet and flow through the observation cuvette. Simultaneously, the light intensity

signal from the photomultiplier tube, transmitted by passing a monochromatic light through the mixed solution in the cuvette observation chamber, is amplified and an output signal proportional to the absorbance (10 volts = 1 absorbance) is generated. The output signal is transmitted as function of reaction time to the oscilloscope or strip chart recorder for display and to an automatic date acquisition system for collection, storage and analysis of the kinetic data.

DATA ACQUISITION SYSTEM

A data acquisition system for rapid kinetic experiments has been developed (8), utilizing the hardware components on loan from U. S. Environmental Protection Agency. A PDB 8M computer with A/D converter, tape drive unit and formatter, analog recorder, oscilloscope, and input/output terminal interfaced to the stopped-flow spectrophotometer provides the complete data acquisition system. Timing for actual data collection is generated through internal computer software with inclusion of A/D conversion time. The sampling time interval can be selected from the range of 1×10^{-4} to 100 sec. depending on the speed of a reaction. A total of 1943 data points can be collected and stored, and therefore, the total sampling time for a reaction can vary from 0.1943 to 1.943×10^{5} sec.

The system software, along with tape drive programs, is stored in core memory. All other machine language subroutines as well as high level programs are stored on tape. User-selected data, special analysis programs, and results are also stored on tape. Typical application of the system begins with a simple initialization from the computer console. After this start-up, software programming provides complete interaction between the user and the Decwriter III or teletype terminal. The user is directed through

the process by a series of decision steps. The initial step is to choose a data file, either existing or new. Upon selecting the desired data file, a sequence of options is initiated, the first one being data collection. If an existing data file is chosen, the decision to write over this data is left open to the user. Should the data collection be negated, the existing data is transferred from the tape to core memory for a series of print and analysis options. If data collection is assumed, various experimental parameters and timing contants are entered. After each run, the user may then decide whether to keep the new spectrum or return to re-initialize data collection for the same data file. A successful experiment may then be catalogued, and results printed out or stored on tape. At this juncture, the user can choose another data file or continue the print and analysis options. Details of the data acquisition system are described in a thesis (8). For all experiments carried out in this project, the kinetic data were preserved on hard paper copies(8,20,22).

GAS CHROMATOGRAPH AND MASS SPECTROMETER SYSTEM

A Hewlett-Packard reporting gas chromatograph (Model 5840A) was utilized in this research to identify products of ozonation and to determine the stoichiometric ratio of the reaction between benzene and ozone (8, 20,22). The system consisting of dual flame ionization detectors is a digital processor based instrument, and can be operated from a keyboard with 53 keys. The keyboard is a part of a terminal module which also includes a chart paper drive and printing mechanisms. The terminal is connected to a mainframe module by a standard ribbon cable which permits a maximum separation between the two modules at about 100 cm. The mainframe houses the injection port column oven detectors, gas flow systems, and electronics. A power fail protection

circuit is built into the power supply, and will maintain all setpoint entries in memory for at least half-an-hour should the power be interrupted.

The gas chromatograph can be operated by setting the injection temperature in the range of 0 to 400°C. The temerature of the detector is normally controlled in the range of 250 to 300°C. Either nitrogen or helium can be used as a carrier gas and flow rate through the two columns can be controlled by pressure regulators. Time programming capabilities for changes in the GC conditions, detector operations, chromatogram presentation, data reduction parameters, etc. are provided by the system.

Several separation columns including OV-17, FFAP and Chromsorb were found to be effective in detections of various hydrocarbons and reaction products in the present research. A separation column in the gas chromatograph is packed with a special material causing separation of different species from a mixture carried by an inert carrier gas. Separation of the compounds is possible because of the adsorption by the special material in the column which has different affinity to different chemical species.

Following separation of individual compounds by the gas chromatograph, a mass spectrometer can be employed to identify each chemical species. In the mass spectrometer, the molecules of the individual species are bombarded by a stream of electrons and then, spectra of positive ion fragments are quantitatively recorded. The positive ion fragments are distinguishable because of mass or mass/charge differences. A Du Pont GC/Mass spectrometer (Model 490-F) located at the Forest Product Utilization Laboratory on the campus was employed to perform analyses of some samples. The utilization of a mass spectrum for identification arises from the fact that the impact of an electron beam upon a given molecular species produces a family of positive particles

whose mass distribution is characteristics of the parent species.

SECTION 5

EXPERIMENTAL PROCEDURES AND ANALYSES

DETERMINATION OF ABSORPTION COEFFICIENT

Preliminary tests were conducted to determine the relationship between the absorbance of an ozone solution measured by the spectrophotometer at a given wave length and the actual concentration of ozone in the solution. The iodometric method was employed to determine concentrations of ozone in aqueous solutions. The oxidation of potassium iodide by ozone results in liberation of iodine which can be titrated by sodium thiosulfate solutions using starch as an indicator. The instantaneous reactions in the solution are as follows:

$$O_3 + 2KI + H_2O \rightarrow O_2 + I_2 + 2KOH \quad (4)$$

$$I_2 + 2Na_2 S_2O_3 \rightarrow Na_2 S_4O_6 + 2NaI \quad (5)$$

In a preliminary experiment, the absorbance of a buffer solution containing dissolved ozone at a fixed pH value and temperature was measured by the spectrophotometer at a given wave length. Simultaneously, a portion of the solution was mixed with a solution containing excess potassium iodide. Since potassium hydroxide was produced, the mixed solution was acidized by sulfuric acid to maintain a pH value of 2 or below. The mixed solution was stirred continuously and titrated by the sodium thiosulfate solution until the yellow color of the liberated iodine nearly disappeared. As the colorimetric end point was approached, starch indicator was added to develop a dark blue color. The titration was continued until the blue color disappeared from the solution. The initial concentration of ozone in the solution, therefore, can be calculated

from the amount of sodium thiosulfate consumed in the titration.

Absorbances of various cocentrations of dissolved ozone measured at a wave length of 270 nm are illustrated in Figure 2. As can be seen from this figure, a linear relationship exists between the absorbance, A, and the ozone concentration, C_A. This result suggests that the Beer's law is valid within the concentration rage of interest.

$$A=\varepsilon b C_A \qquad (6)$$

In the above equation, the molar absorptivity or absorption coefficient, ε, at 270 nm with light path b=2 cm, is obtained from the slope of the straight line as 1,650 M^{-1} cm^{-1}. Figure 2 demonstrates that the linear relationship prevails for all of the data measured in solutions of different pH values. Also, temperature changes have negligible effect on the measured absorbances. The experiments were conducted at various wave lengths yielding the absorption coefficients or molar absorptivities as follows :

wave length, nm	245	260	270	280
absorptivity, M^{-1} cm^{-1}	2,070	3,590	1,650	820

The above results are in good agreement with those reported in the literature (1,12).

The kinetics of ozonation reactions were studied at 270 nm for benzene-ozone systems, and at 280 nm for toluene-ozone systems to avoid exhibition of significant absorbances by the hydrocarbons in the solutions. For other reactions investigated in this research, the kinetic data can be measured at 245 or 260 nm without trace of absorbance exhibited by the hydrocarbon reactants or reaction products.

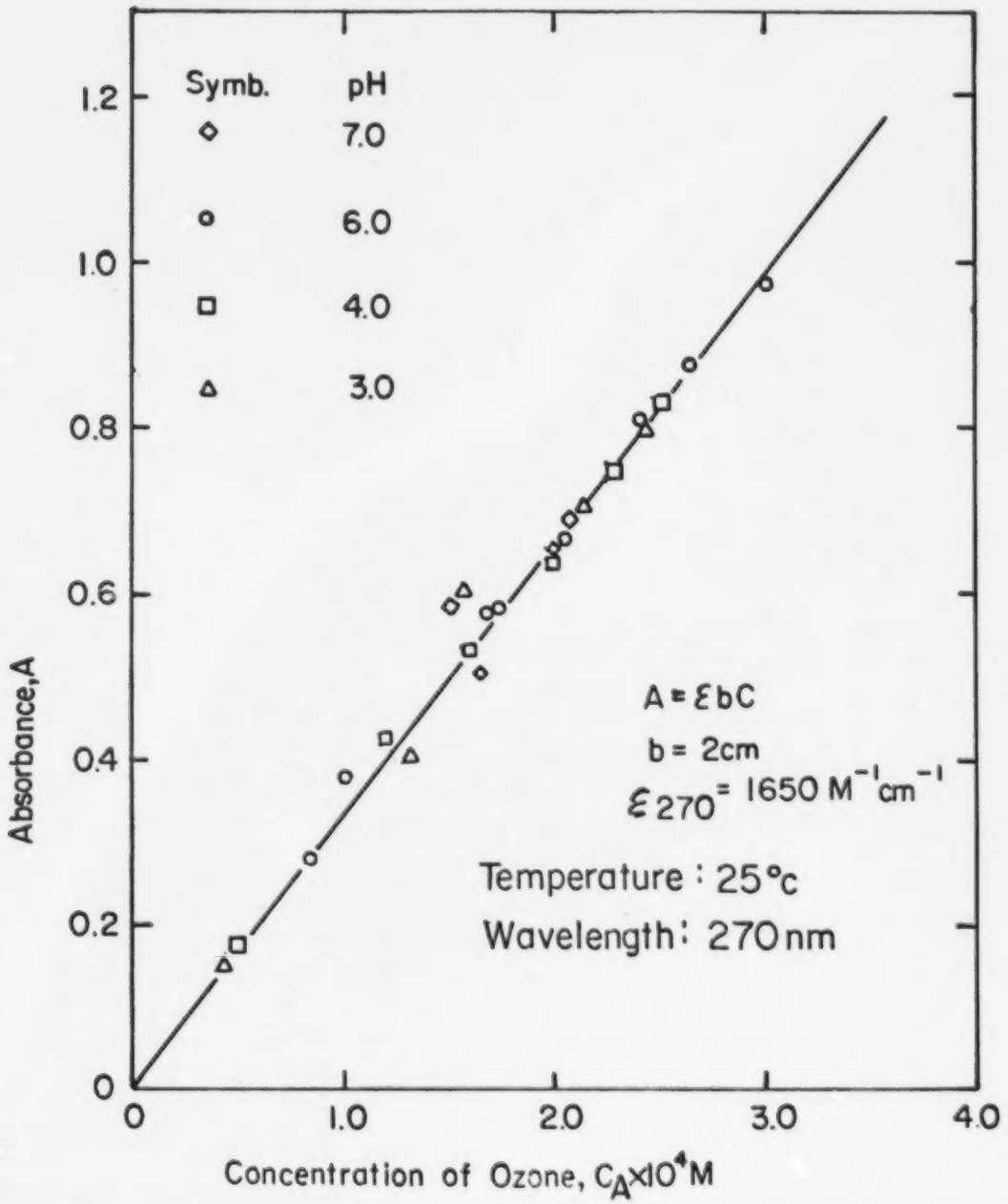


Figure 2. Relationship Between Absorbance And Ozone Concentration

KINETIC EXPERIMENTS

As described in the previous section, a stopped-flow spectrophotometer system was utilized for the kinetic measurements. An aqueous solution of ozone was prepared by bubbling a mixture of ozone and oxygen, produced from the ozonator, into a buffer solution contained in a Corning 3-040 gas washing bottle. The washing bottle was immersed in an isothermal bath to maintain a desired temperature. A hydrocarbon solution was prepared from the buffer solution of identical pH value according to the procedures discussed in Section 4. The two solutions of ozone and hydrocarbon were stored in separate drive syringes in the stopped-flow spectrophotometer system prior to an experiment, and a constant temperature was maintained in the flow section by coolant (water) circulation. By activating the flow actuator, the two reactants were mixed rapidly in the mixing jet and allowed to flow through the observation cuvette where the mixed solution was stopped abruptly. Absorbances of the mixed solution (as voltage in the output signals, 10 vdc = 1 absorbance unit) were sampled at a fixed wave length in a time interval varying from 1×10^{-4} to 100 sec. and stored in the PDP 8 M computer memories. The data acquisition system developed in this work was applied using regression analyses to correlate the experimental data. With few exceptions, the experiments were carried out in solutions with large excess of hydrocarbons to facilitate analyses of the kinetic data.

Both the integration and the initial rate methods can be employed to analyze the kinetic data. In the decomposition reaction of ozone (A) accompanied by an ozonation reaction between ozone and a hydrocarbon (B) in liquid phase, the overall reactions can be expressed in the following forms:

$$A \xrightarrow{k_1} P_s \qquad (7)$$

$$A + B \xrightarrow{k2} Q_s \qquad (8)$$

The rate of depletion of ozone in the above simultaneous reactions can be written as

$$-dC_A/dt = k_1 C_A^{\ell} + k_2 C_A^m C_B^n \qquad (9)$$

where C_A and C_B are concentrations of the ozone and hydrocarbon, respectively, in the solution. Rates of decomposition of ozone were determined in an earlier work and the order of decomposition, ℓ, was found to be three-halves (12). The rate constant, k_2, and orders of ozonation reaction, m and n, can be determined by analyzing the absorbance data carried out in this research.

The experimental systems encountered in this research can be classified into several cases for analyses of the absorbance data. Methods of analyses have been developed assuming that the hydrocarbon is present in large excess at a constant concentration, C_{BO}, in the solution. If the order with respect to ozone concentration in the decomposition is identical to that in the ozonation reaction, ℓ=m, then equation (9) can be rewritten as

$$-dC_A/dt = k' C_A^m \qquad (10)$$

where the apparent rate constant is

$$k' = k_1 + k_2 C_{BO}^n \qquad (11)$$

Integration of equation (10) yields,

$$\ln C_A/C_{AO} = -k't, \text{ for } m=1 \qquad (12)$$

and

$$(C_A/C_{AO})^{-m+1} = 1 - k'(1-m)C_{AO}^{m-1}t, \text{ for } m \neq 1 \qquad (13)$$

In the above equations, C_{AO} is taken as the concentration of ozone at a time (0.0005 to 0.002 milliseconds) where complete mixing (>%9.5%) of the reactants in the solution is achieved. The above equations also are applicable to a system in which the ozonation reaction is much faster than the decomposition

reaction regardless of any difference in reaction orders, ℓ and m. For this case, the decomposition rate constant, k_1, can be ignored in the above equations.

To apply the above integration method for analysis of absorbance data obtained from a given experiment, it is necessary to establish a relationship between the absorbance and concentration of ozone in the solution. If no appreciable absorbance is exhibited by any chemical species other than ozone in the solution, then the concentration of ozone can be computed from equation (6) using the known value of the absorption coefficient for a given wave length. For cases where absorbances of ozone as well as reaction products are significant and the ozonation reaction is controlled by an overall step indicated by equation (8) with negligible effect of the decomposition reaction, the concentration of ozone can be shown to vary with the absorbance in the following form (6,13):

$$C_A(t)/C_{AO} = [A(t)-A(\infty)]/[A(o)-A(\infty)] \qquad (14)$$

where $A(\infty)$ is the asymptotic absorbance of the solution measured after completion of the ozonation reaction. By employing the relationship given in equation (14), the dimensionless concentration can be plotted against the reaction time on a semi-logarithmic or regular scale according to equation (12) or (13). Regression analyses can be utilized to find a best correlation of the experimental data yielding the reaction order m and the apparent rate constant, k'. By plotting $(k'-k_1)$ versus the initial hydrocarbon concentration, C_{BO}, on a logarithmic scale, a straight line can be obtained where the slope gives the order with respect to the hydrocarbon concentration, n. Thus, the ozonation rate constant, k_2, can be computed from the intercept or equation (11).

For a system controlled by multiple reaction steps, a quantitative relationship between the concentration of ozone and absorbance of the solution has not been established. Nevertheless, the initial rate method may be applicable if it is permissible to approximate the rate change in concentration of ozone by that of absorbance.

$$dC_A/dt = dA/dt, \text{ at } t=o \qquad (15)$$

At the initial time, equation (10) can be rewritten in the following form if the decomposition reaction can be ignored

$$\ln(-dC_A/dt) = \ln k' + m \ln C_{AO}, \text{ at } t=o \qquad (16)$$

By plotting on a logarithmic scale, the initial rate against the initial concentration of ozone for various experiments conducted in solutions of identical pH value and temperature, a straight line can be drawn. The intercept and slope of the linear plot yield k' and m, respectively. The ozonation rate constant, k_2, and the order with respect to hydrocarbon concentration, n, then can be obtained from the method discussed earlier.

IDENTIFICATIONS OF OZONATION PRODUCTS

The gas chromatograph with flame ionization detector was utilized to separate products of ozonation. Both chromosorb and FFAP columns were used to detect products of reactions between ozone and olefinic compounds. For analysis of products in the benzene-ozone reaction, an OV-17 column was found to be most effective. To achieve best results in separation of the reaction products, the column temperature was programmed at a rate of about 5°C/min. from 80 to 150°C and the flow rate of carrier gas (nitrogen) was set at 20-25 ml/min. Injection and detector temperatures were controlled at 170 and 280°C, respectively. Several runs were made to find the optimum slope sensitivity and attenuation.

Injection samples were prepared by several methods using either distilled water or buffer solutions. A solution with a known quantity of hydrocarbon was prepared first. By bubbling ozone gas or by mixing a solution containing dissolved ozone in the hydrocarbon solution, ozonation products were formed. Then, the reaction products were extracted by ACS grade ether five times using a small volume in each extraction with vigorous agitation. Following the removal of the ether layer, the extracted solution was concentrated to about 5 ml by evaporation at room temperature. Samples of the concentrated solutions were injected into the gas chromatograph using a sample volume of 2 μℓ for each injection, and a gas chromatogram was recorded from the analysis.

Standard solutions were prepared by dissolving appropriate amounts of hydrocarbons or known reagents in the distilled water or buffer solutions. Using the same separation condition, chromatograms of these standard solutions were obtained, and retention times compared with those of unknown products in the ozonized solutions. Also blank samples were analyzed to detect any contaminants in the distilled water or buffer solutions.

The concentrated samples also were used to produce the mass spectra of the reaction products from the mass spectrometer following a separation by the gas chromatograph. The mass spectra were compared with those of known chemical species for positive identifications of individual products of the ozonation reactions.

DETERMINATIONS OF STOICHIOMETRIC RATIOS OF REACTIONS

The gas chromatograph was utilized for quantitative determination of concentrations of a hydrocarbon in an aqueous solution before and after ozonation reaction. A 5% FFAP glass column with a length of 6 feet was employed. To obtain the best results, the flow rate of helium (a carrier gas)

was adjusted at about 30 ml/min., and column temperatures varied from 90 to 150°C. The injection and detector temperatures were selected at 150 and 280°C, respectively.

Preliminary tests were first conducted to determine chromatographic areas at various concentrations or quantities of hydrocarbon in solutions. For a test solution, the initial concentration of hydrocarbon was determined before reaction. An ozone solution was then prepared and its initial concentration measured by the spectrophotometer. Simultaneously, a known volume of the ozone solution was mixed with an equal volume of the hydrocarbon solution, and the ozonation reaction allowed to proceed to completion. The hydrocarbon was prepared in excess to completely deplete the dissolved ozone in the mixed solution. By subtracting the amount of ozone decomposed during the ozonation reaction, the net quantity of ozone depleted in the ozonation reaction can be computed. Also, the residual hydrocarbon in the solution after reaction was determined by the gas chromatograph to estimate the net amount of hydrocarbon consumed by the dissolved ozone. Thus, the ratio of moles of hydrocarbon to ozone required in the ozonation reaction can be computed.

SECTION 6

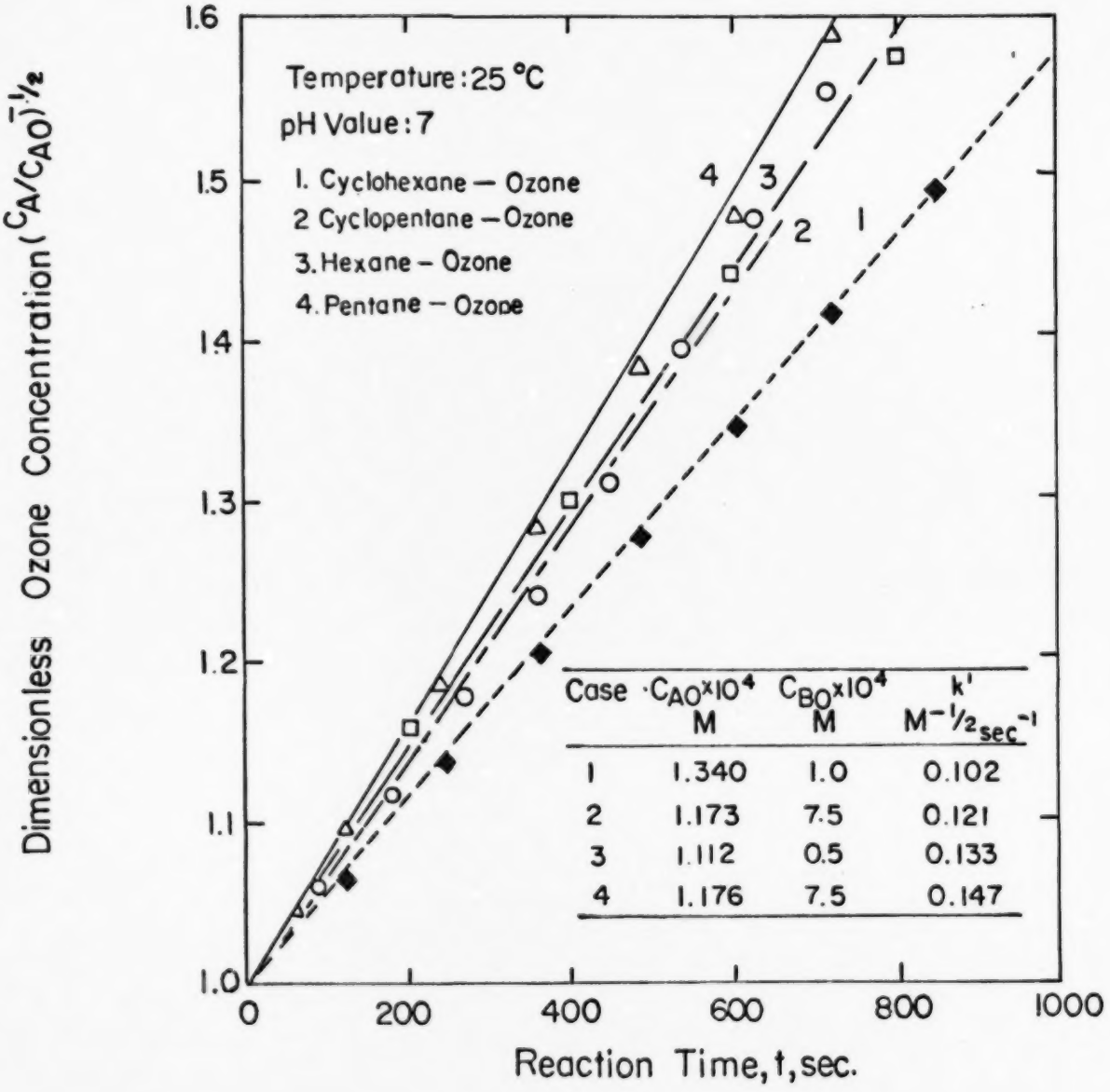
RESULTS AND DISCUSSION

OXIDATION OF SATURATED HYDROCARBONS

Oxidation of several saturated hydrocarbons including cyclohexane, cyclopentane, hexane, and pentane by ozone in aqueous solutions was investigated. Rates of the oxidation were measured in solutions of pH range between 2 to 9 at temperatures varying from 5 to 35°C. The ionic strength of all solutions was maintained at 0.1. In these systems, no absorbance was detected for any chemical species other than ozone, and therefore, the concentration of ozone is directly proportional to the absorbance of a solution as discussed in the previous section.

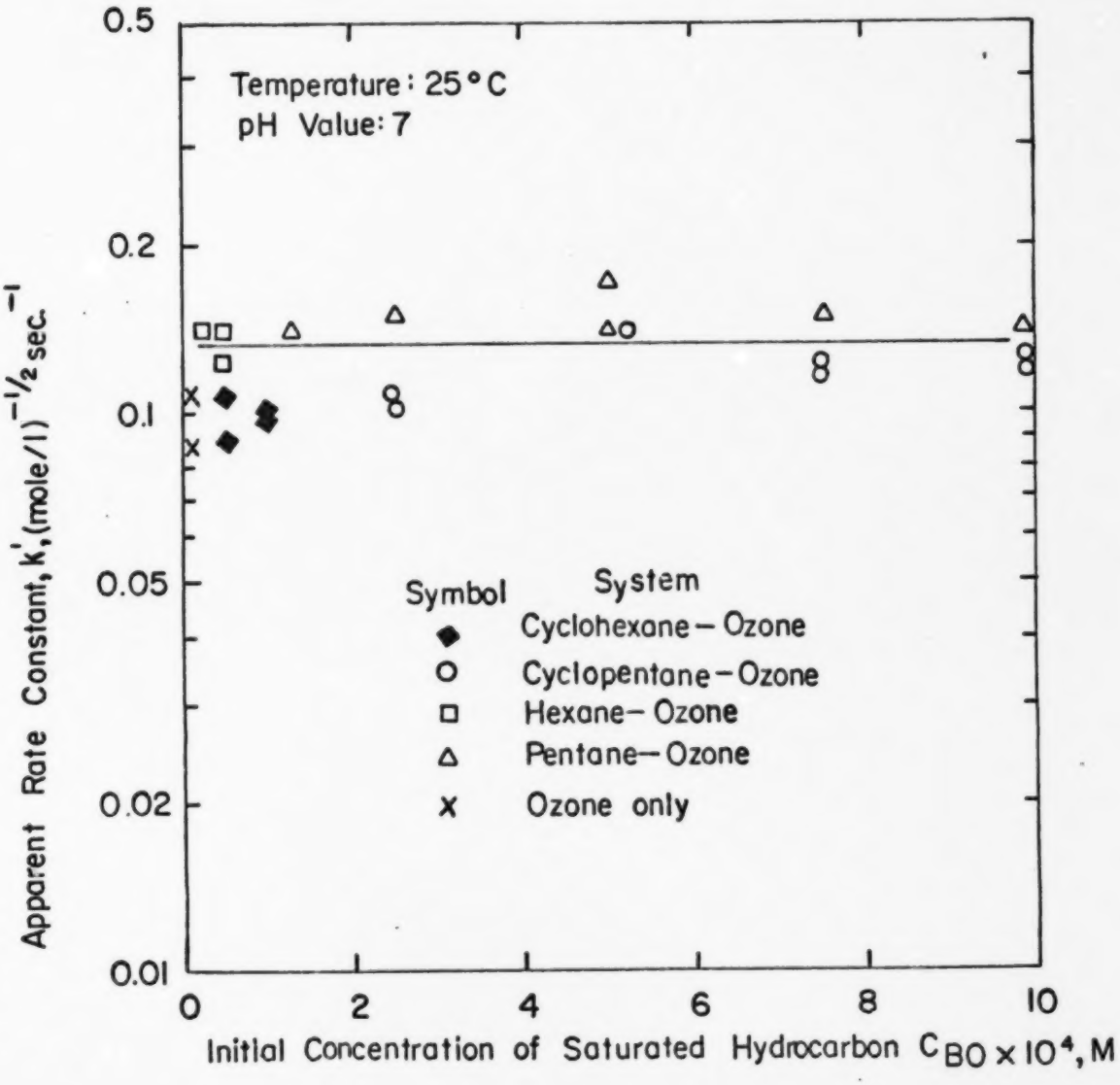
As illustrated in Figure 3, the concentration data for these systems were best fitted by three-halves order kinetics with respect to ozone concentration. This kinetics of reaction is identical to that of decomposition of ozone in absence of any contaminant (1,7,12). Also, the apparent rate constants calculated for these systems are nearly identical to the rate constants for decomposition reactions at the same conditions of experiments as shown in Figure 4. These results suggest that the ozonation reactions were insignificant compared with the decomposition reaction of ozone in the solutions. The ozonation rate constant, therefore, is nearly zero, and the apparent rate constant given in equation (11) also represents the decomposition rate constant for these systems. This conclusion is supported by results obtained at various temperatures and pH values of solutions (20). Attempts were made to detect

Figure 3. Concentration Profiles In Saturated Hydrocarbon-Ozone Reactions



Case	$C_{AO} \times 10^4$ M	$C_{BO} \times 10^4$ M	k' $M^{-1/2} sec^{-1}$
1	1.340	1.0	0.102
2	1.173	7.5	0.121
3	1.112	0.5	0.133
4	1.176	7.5	0.147

Figure 4. Influences of Concentration of Saturated Hydrocarbon on Rate Constant



possible products of reaction formed in the solutions by the method of gas chromatography, but no trace of any chemical species other than the hydrocarbon reactants was found. The above results confirmed the conclusion drawn in the leterature (17) that the saturated hydrocarbons are not reactive with ozone.

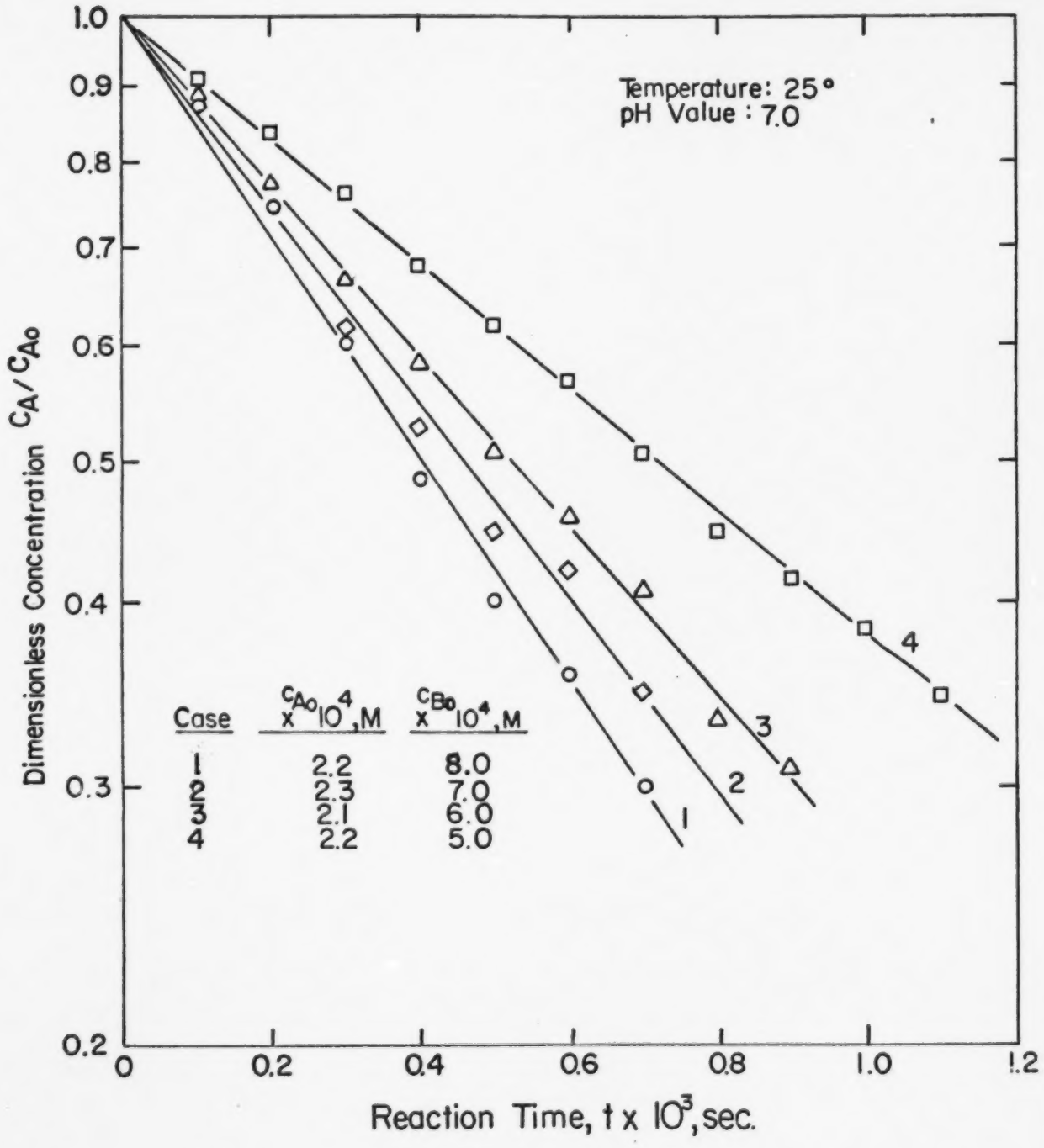
OZONATION OF OLEFINIC COMPOUNDS

Unsaturated hydrocarbons can form organic aerosol when reacting with ozone, and cyclic olefins appear to be one of the most important class of organic aerosol precursors. Although very little information is available in the literature concerning oxidation rates of olefinic compounds in aqueous phase, the second order rate constants for the ozonation reactions in vapor phase have been reported to vary form 3×10^3 to 4×10^4 ℓ/mole-sec. at room temperature (2, 16,17).

Reactions between ozone and cyclohexene, cyclopentene and 1-pentene were investigated in this research. The kinetics of the oxidation of cyclohexene in aqueous solutions of pH values varying from 3 to 7 at different temperatures was studied extensively and the kinetic data are tabulated elsewhere (8). Products of the reactions were separated by the gas chromatograph using several glass columns.

The stoichiometric ratio of ozonation of cyclohexene was determined to be unity by the procedures described in the previous section. As demonstrated in Figure 5, the reactions in neutral solutions at various initial concentrations of cyclohexene were very fast with half lives of less than one millisecond at 25° C. Therefore, the rate of decomposition is very slow compared with the ozonation reaction and can be neglected in analyzing the kinetic data. Since cyclohexene and the reaction products exert no contribution to the absorbance at 245 nm, the Beer's law is applicable, and equations (12) and (13) can be utilized to correlate absorbances measured during a reaction.

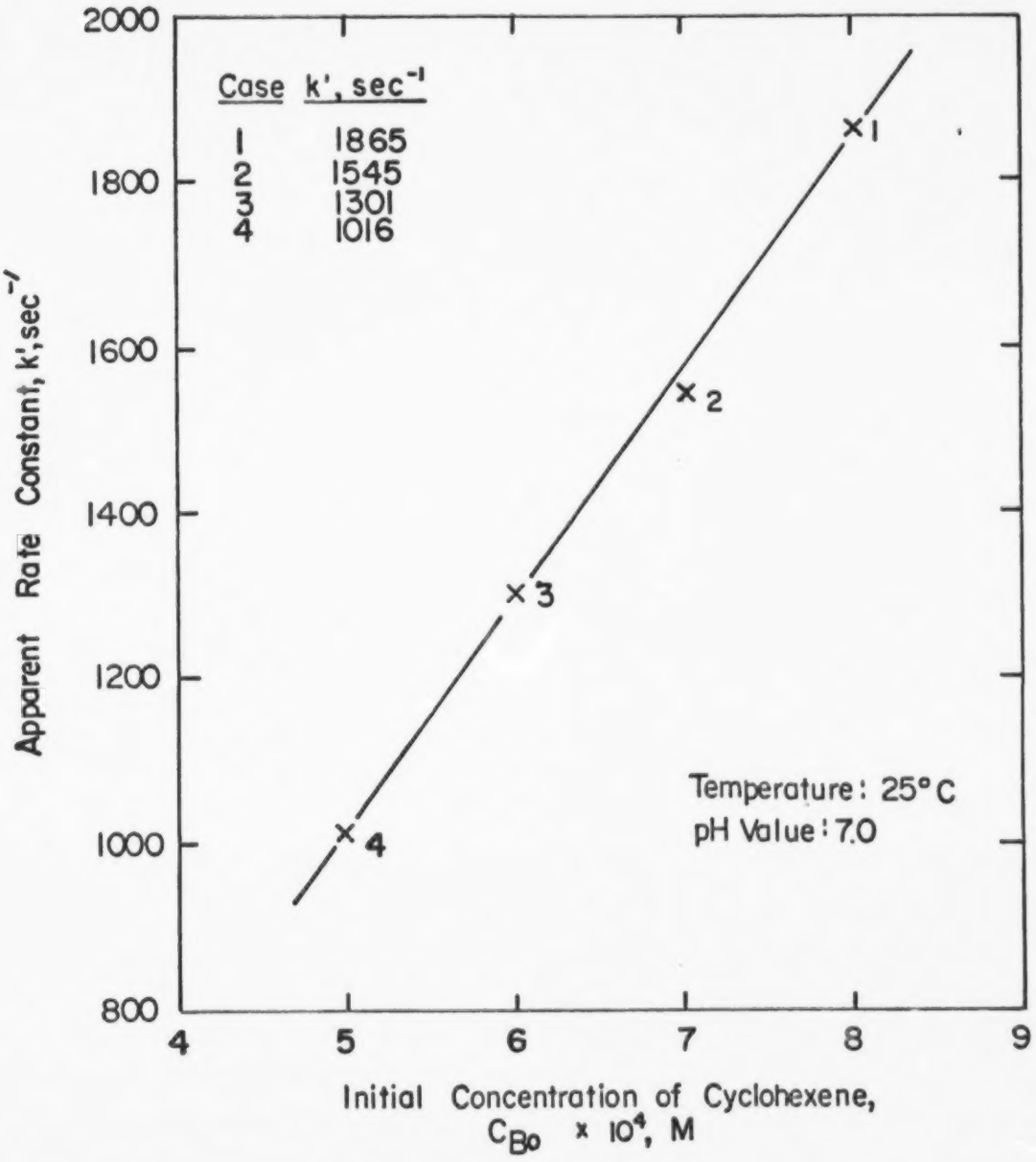
Figure 5. Concentration Profiles in Cyclohexene-Ozone Reactions



Regression analyses revealed that the data were best fitted by first order kinetics (m = 1) as demonstrated in Figure 5. Under this condition. the apparent rate constant, k', can be calculated from a semi-logarithmic plot of the dimensionless concentration versus time in accordance with equation (12). A plot of the apparent rate constant against the initial concentration of cyclohexene, C_{Bo}, in Figure 6 gives a straight line. This indicates that the ozonation reaction was first order with respect to the cyclohexene concentration (n = 1) as can be seen from equation (11). For all reactions in neutral solutions at 25 ^{o}C, the average ozonation rate constant is calculated to be 3.33×10^{6} 1/mole-sec. with an average standard deviation of 16%.

The kinetic experiments for ozonation of cyclohexene were carried out at various temperatures and pH values for a total of more than 80 experimental runs (8). In addition to most cases in which cyclohexene was maintained in excess in the solutions, some experiments were conducted at intial concentrations of ozone nearly indentical or higher than those of cyclohexene. Several methods of analyses described in the literature (6,8) were employed to correlate the kinetic data. All analyses for experiments of different initial concentration ratios of ozone to cyclohexene gave consistant results. The average second order rate constants decrease slightly with the pH value as shown in Figure 7 and Table 2. Also, the calculated results demonstrate that the ozonation rate was not significantly affected by temperature variation. This might be attributed to the fact that the double bond in the olefinic compound is extremely vulnerable to attack by ozone. Therefore, the operating conditions of a reaction system such as pH value and temperature exert very little influences on the rate of ozonation. Several products of the ozonation were formed in the solutions and

Figure 6. Dependence of Apparent Rate Constant On Initial Cyclohexene Concentration



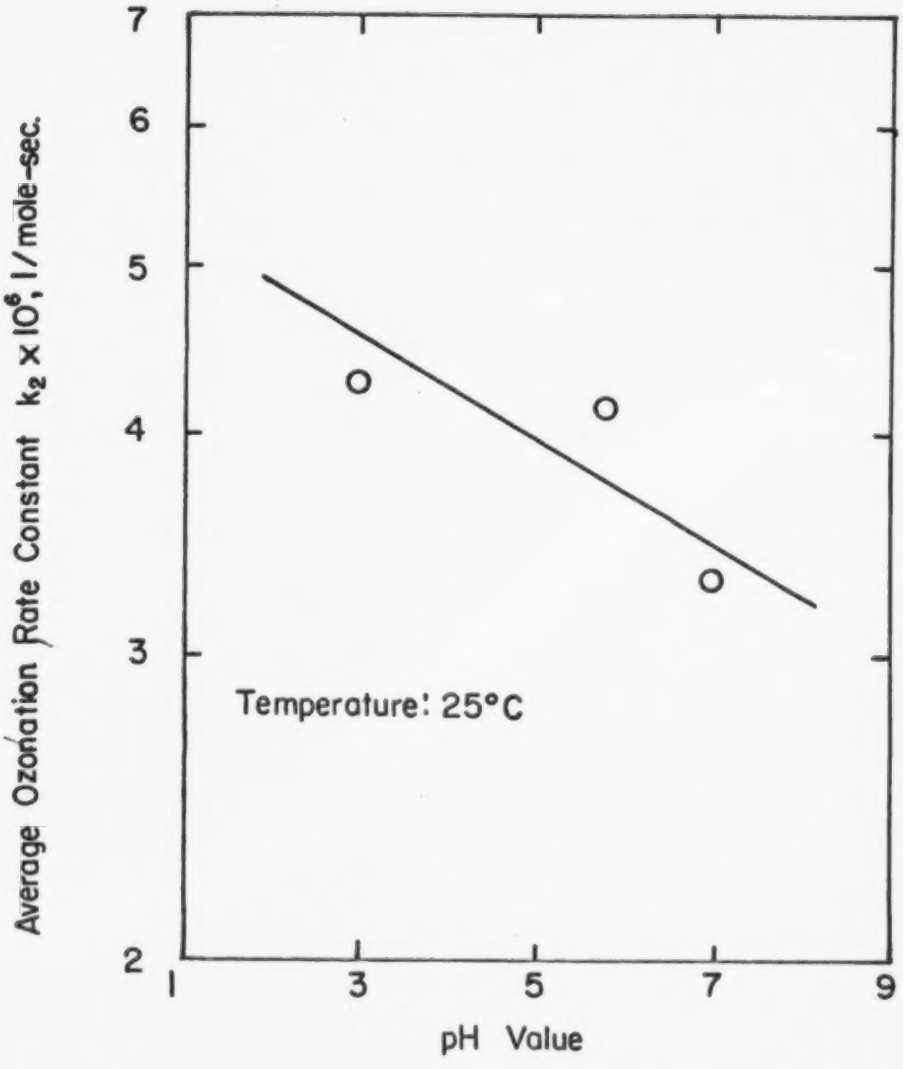


Figure 7. Average Ozonation Rate Constants for Cyclohexene - Ozone Reactions

TABLE 2. REACTION ORDERS AND AVERAGE RATE CONSTANTS FOR CYCLOHEXENE-OZONE SYSTEMS

pH Value	Temperature, °C	Order with respect to Ozone(m)	Cyclohexene(n)	Average Rate Constant, k_2, $M^{-1}s^{-1}$
3.0	25.0	1.0	1.0	4.30×10^6
5.8	25.0	1.0	1.0	4.14×10^6
7.0	25.0	1.0	1.0	3.33×10^6

separated by a glass column in the gas chromatograph. A positive identification of the individual species, however, has not been achieved.

Reactions between ozone and cyclopentene and pentene were found to be faster than the ozonation rate of cyclohexene. Although many attemps were made, quantitative information on the kinetics of reactions could not be obtained because of limitations of the stopped-flow apparatus. On the basis of the results calculated for the cyclohexene-ozone reactions, the second order rate constant for cyclopentene-ozone and pentene-ozone reactions is estimated to be of the order of 1×10^7 1/mole-sec. Using a 5% FFAP and a chromosorb 101 glass columns in the gas chromatograph, acetic acid, acetaldehyde and butyraldehyde were detected as products of ozonation of cyclopentene and pentene in the solutions. In addition, several compounds with molecular weights ranging from 82 to 249 were traced but identities of the individual compounds have not been established. Although, the formation of high molecular compounds has not been reported in the ozonation reactions in vapor phase, the acids and aldehydes were detected (16).

It should be noted that the above olefinic compounds are known to be reactive with ozone in vapor phase. The second order rate constants for the reactions in vapor phase ranged from 3×10^3 to 4×10^4 1/mole-sec, at room temperature as reported in the literature (16). Therefore, the ozonation of an olefinic compound in an aqueous solution is many times faster than the reaction in vapor phase. Experiments were conducted by several investigators (19,25) to study ozonation of olefinic compounds in carbon tetrachloride solutions. The second order rate constant at 0°C was reported (19) to be 0.96×10^5 1/mole-sec. for cyclohexene-ozone reaction. Williamson and Cvetanovic (25) gave the second order rate constants of 0.76×10^5 1/mole-sec.

for 1-pentene-ozone and 1-hexene-ozone reactions at 25°C and 2.0×10^5 1/mole-sec. for cyclopentene-ozone reaction in CCl_4 solutions at 27.4°C. Although a direct comparison of the experimental data has not been possible, the results of this study seem to suggest that the ozonation reactions in aqueous solutions are faster than in CCl_4 solutions.

OZONATION OF AROMATIC COMPOUNDS

Rates of reactions between ozone and benzene and toluene were measured in this research. The stoichiometric ratio of benzene to ozone in the ozonation reactions was found to vary from 0.97 to 1.26. Thus, it may be reasonable to consider the ratio as unity for benzene-ozone reactions in aqueous solutions. To study kinetics of oxidation of benzene, a total of 52 experiments were carried out at 5 to 35°C in aqueous solutions of pH values varying from 3 to 7. The ionic strength was maintained at 0.1 in all solutions. Absorbances of the solution during a reaction were measured at a constant wave length of 270 nm. Preliminary tests indicated that at this wave length, the absorbance of benzene in dilute solutions was negligible. The kinetic data are tabulated elsewhere(22). For the toluene-ozone reaction, the experiments were conducted at 25°C in solutions of various pH values. The absorbances during a toluene-ozone reaction were traced at 280 nm to avoid exhibition of significant absorbance by toluene in the solution.

Typical absorbance curves for oxidation of benzene are illustrated in Figures 8 and 9 for reactions conducted in acidic and neutral solutions, respectively. As can be seen from these figures, benzene was very reactive with ozone, especially in the neutral solutions. The half life of ozone in solutions without any contaminant (7,12) was at least 100 times longer than that in benzene solutions at the corresponding pH value and temperature.

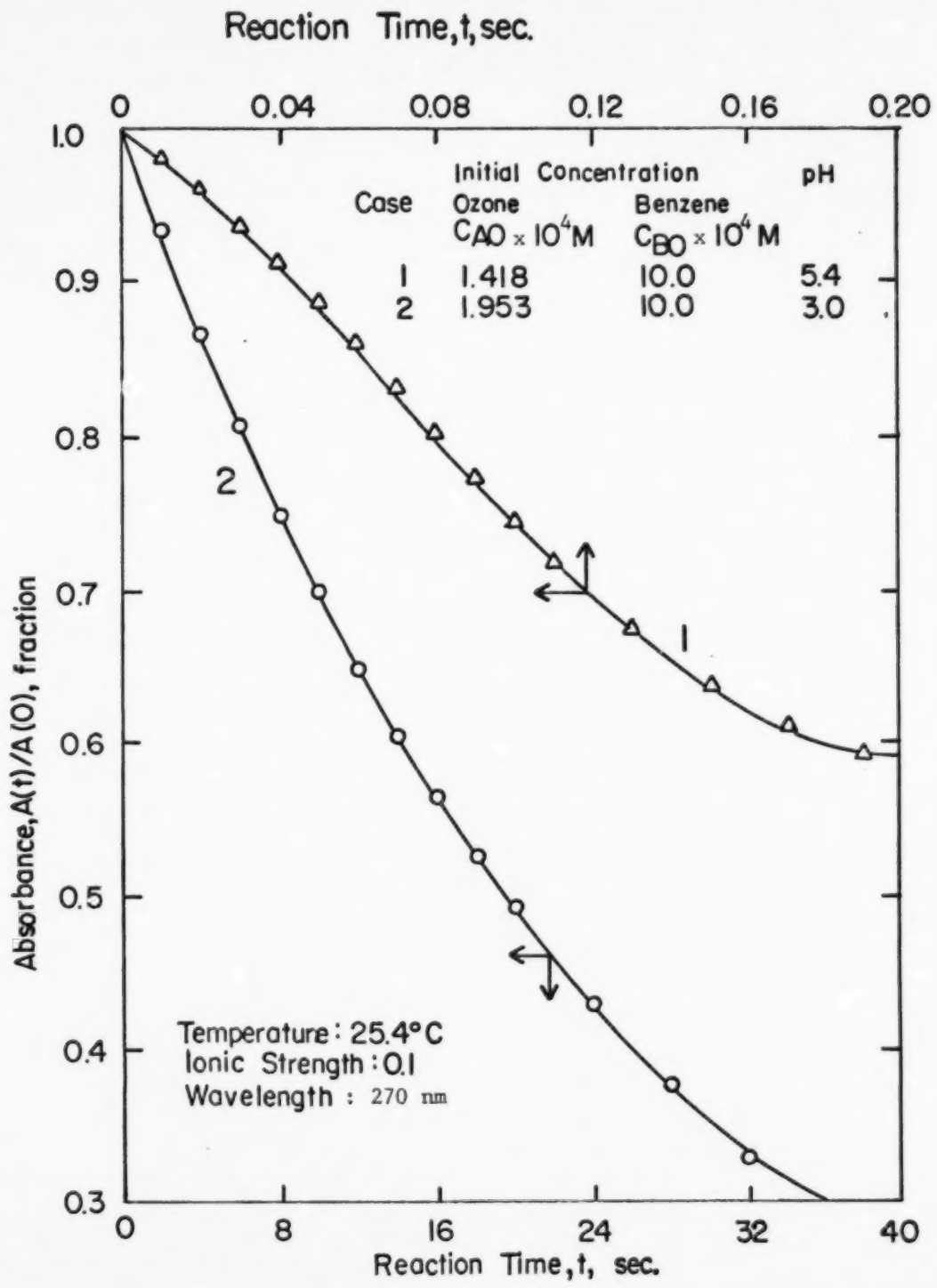


Figure 8. Absorbance Curves For Benzene - Ozone Reactions In Acidic Solutions

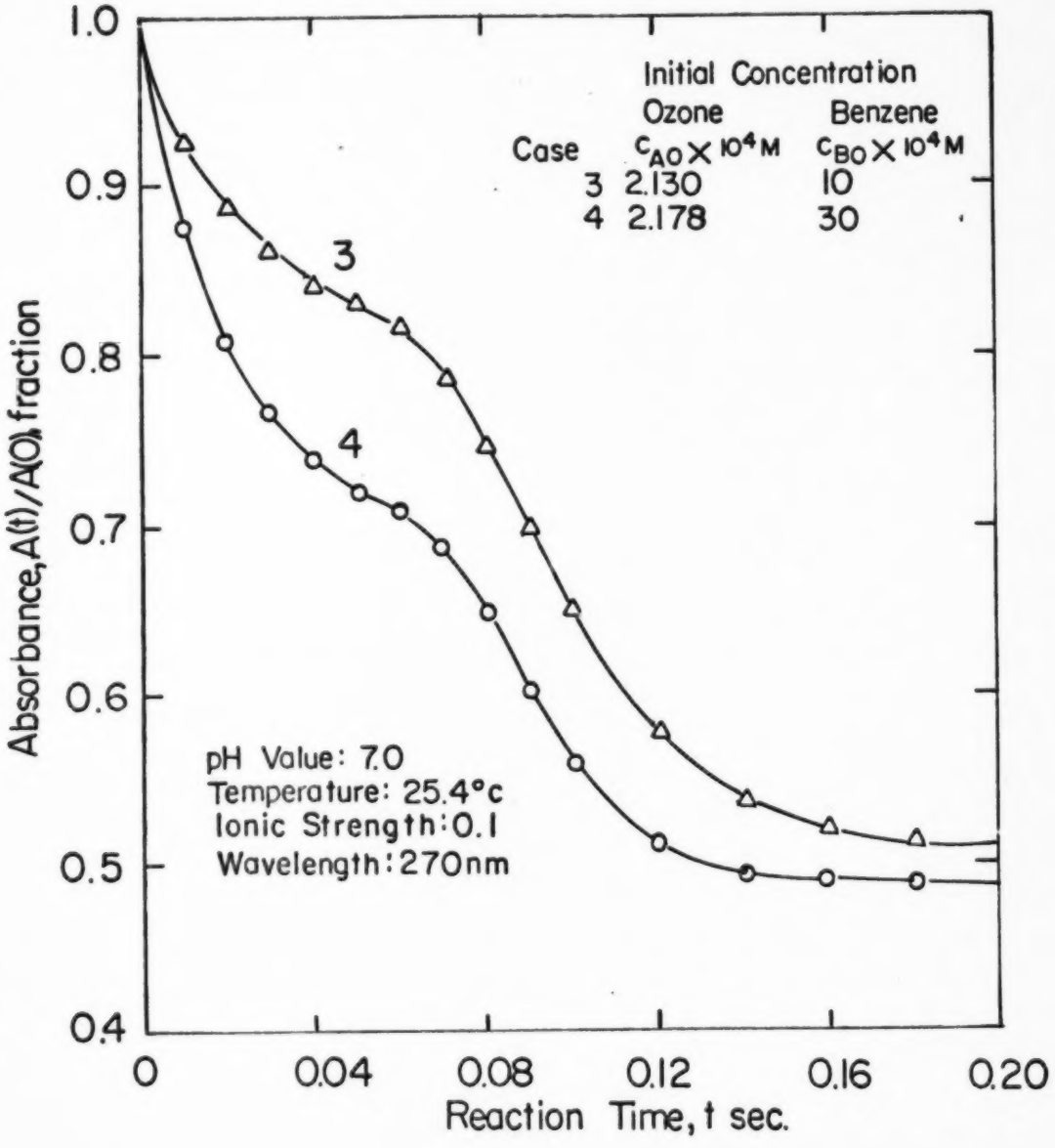


Figure 9. Absorbance Curves For Benzene - Ozone Reactions In Neutral Solutions

Therfore, the rate of decomposition of ozone was very slow and could be ignored in computing the rate of ozonation between benzene and ozone as mentioned earlier. Although no appreciable absorbance of benzene in solutions was detected, the absorbance of the solutions after a reaction was significant. This indicates that the absorbance was exhibited by certain species of the reaction products. In acidic solutions, the absorbance declined smoothly with reaction time and approached an asymptotic value as demonstrated in Figure 8. In neutral solutions as shown in Figure 9, however, the absorbances changed in two distinct stages before approaching a final asymptotic value. These results seem to suggest that the reaction in the neutral solutions was controlled by mechanisms different from that in the acidic solutions.

In the acidic solutions, the ozonation reaction was controlled by an overall step. Under this condition, the absorbance is related to the concentration of ozone by the relationship given in equation (14). Regression analyses were performed, and, as demonstrated in Figure 10 for some typical runs, the order with respect to ozone concentration was found to be one-half (m=1/2). The apparent rate constants, k', for all experiments in the acidic solutions were plotted against initial concentrations of benzene on a logarithmic scale as dictated by equation (11). Again, the slope and intercept of a plot can be determined by regression analyses. The order with respect to the concentration of benzene varied from 0.3 to 0.7, and therefore, the reactions can be considered as one-half order (n=1/2). The first order rate constant for the ozonation of benzene, k_2, can be computed from equation (11) as tabulated elsewhere (22). The average rate constants at given pH values and temperatures are listed in Table 3. The maximum deviation of the individual rate constants from the average values is 32%. For systems with a pH value of

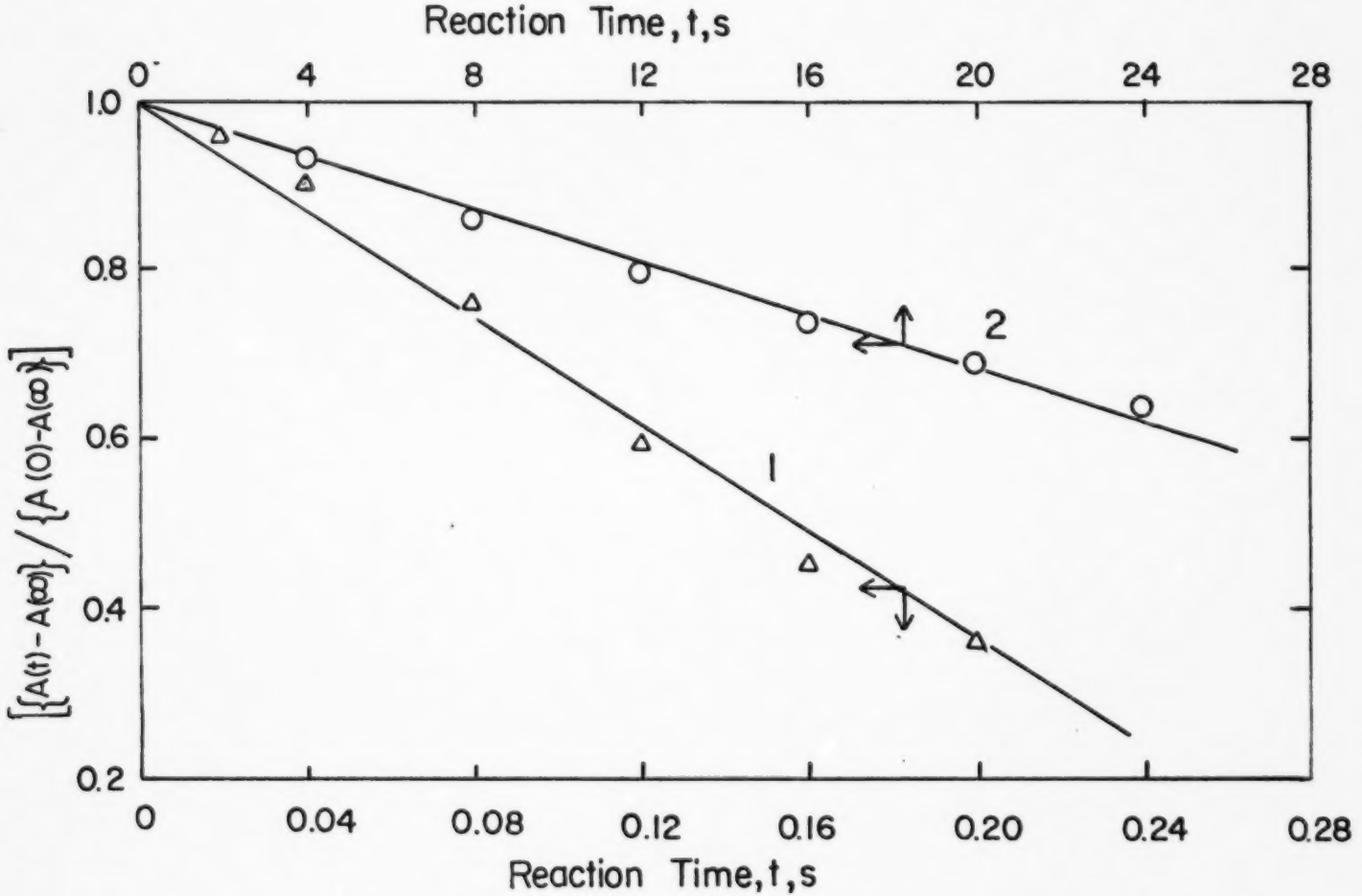


Figure 10. Determination of Reaction Order With Respect to Ozone In Benzene - Ozone Reactions

TABLE 3. REACTION ORDERS AND AVERAGE RATE CONSTANTS FOR BENZENE - OZONE SYSTEMS

pH Value	Temperature, °C	Order with respect to Ozone(m)	Benzene(n)	Average Rate Constant, k_2,s^{-1}
3.0	5.0	0.5	0.5	0.00055
3.0	15.0	0.5	0.5	0.0014
3.0	25.4	0.5	0.5	0.0120
3.0	35.0	0.5	0.5	0.0121
5.4	25.4	0.5	0.5	2.67
7.0	5.6	1.0	0	7.83
7.0	15.5	1.0	0	12.13
7.0	25.4	1.0	0	12.20

3, the average rate constant varied from 0.00055 to 0.0121 sec^{-1} as the temperature increased from 5 to 35°C. At a fixed temperature of 25°C, the rate constant increased from 0.012 to 2.67 sec^{-1} as the pH value changed from 3.0 to 5.4.

For the reactions in neutral solutions, the integration method is not applicable because of complexity of the reaction mechanisms. Nevertheless, the absorbance of a reacting solution during early life is contributed mainly by ozone. Under this circumstance, the depletion rate of ozone given in equation (15) in the initial period can be expressed in terms of a second-order formula from expansion of Taylor series (22). The kinetic data measured in the neutral solutions were analyzed by the initial rate method outlined in the previous section. As illustrated in Figure 11, the absorbance of a solution depleted fairly linearly during the very early period of the reaction, Thus, equation (15) can be utilized to compute the initial rate of reaction. By plotting the initial rate against the initial concentration of ozone on a logarithmic scale, the order with respect to ozone concentration was found to be unity (m=1) from the slope of linear plot. The apparent rate constants, k', estimated from equation (10), were not very sensitive to the initial concentration of benzene. Therefore, the reaction can be considered zero order with respect to benzene concentration, and the reaction rate constant is identical to the apparent rate constant as dictated by equation (11). As indicated in Table 2, the average first order rate constant in the neutral solutions changed from 7.8 to 12.2 sec^{-1} as temperature increased from 5 to 25°C.

Kinetics of ozonation of polyalkyl benzenes in carbon tetrachloride and acetic acid at 25°C were investigated by Nakagawa, et al. (15). Rate constants were calculated by these authors assuming that the reactions were

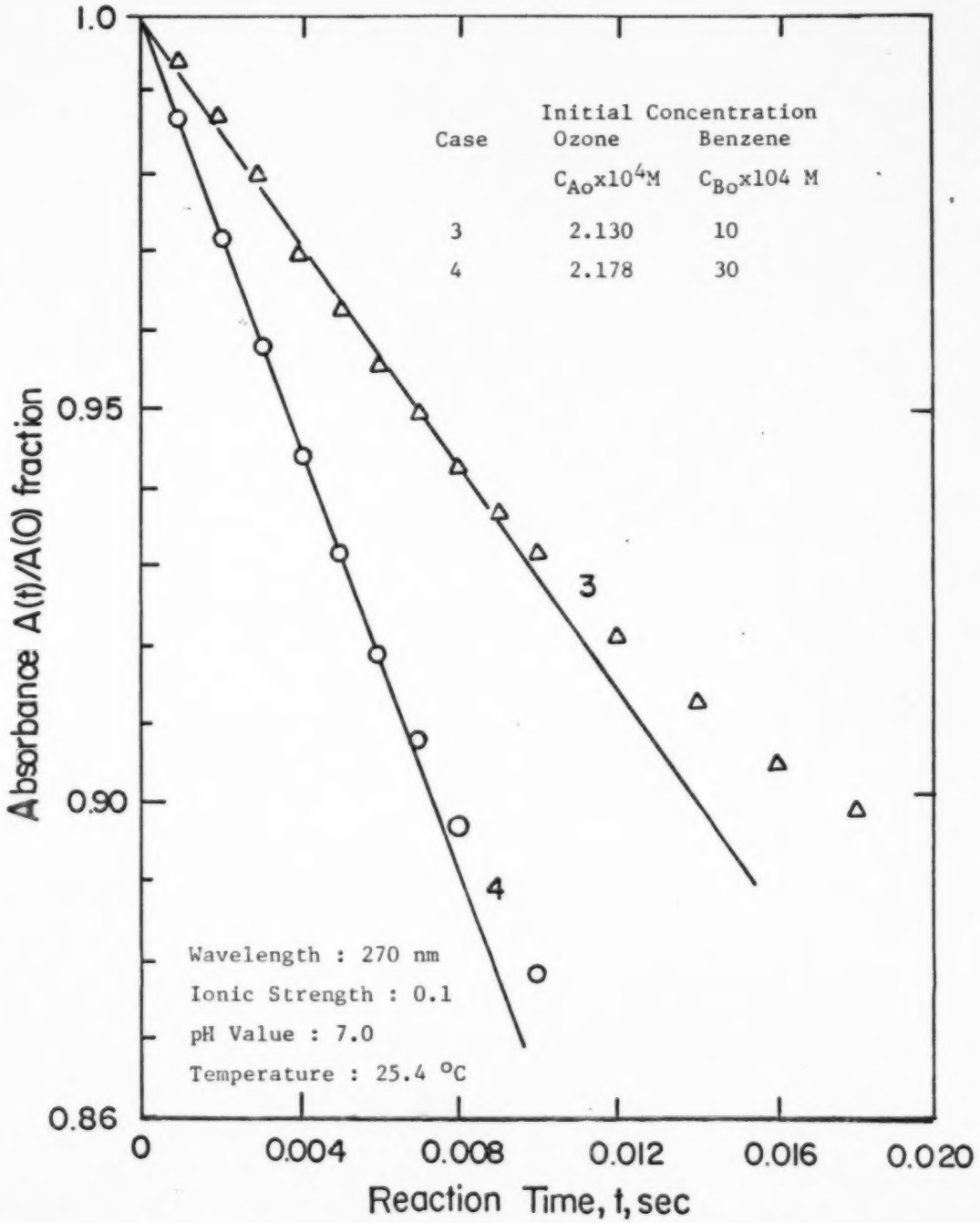


Figure 11. Change of Absorbance With Reaction Time in Benzene - Ozone Reactions

second order (first order in ozone and in aromatic hydrocarbon). The ozonation reactions with benzene were slow with the second order rate constant of 0.028 in CCl_4 and 0.091 1/mole-sec. in CH_3COOH. In the present research, however, the ozonation reaction was found to be very fast especially in neutral solutions. The half life of ozone in neutral solutions was less than 0.2 sec at 25°C, and the first order rate constant was 12.2 sec^{-1} as stated above. This rate constant of 12.2 sec^{-1} is equivalent to about 1×10^5 1/mole-sec. on the basis of second order correlation. Therefore, the reaction rate in aqueous media was at least one million times faster than the rate in carbon tetrachloride or in acetic acid. Hoigne and Bader (10) also measured rates of ozonation of benzene in aqueous solutions at 258 nm, and reported a second order rate constant of about 8 1/mole-sec. Because of the significant absorbance of benzene exhibited at 258 nm, the measurements of the depletion rate of ozone from absorbance changes might have been obscured in their study.

Although the oxidation of benzene proceeded at a moderate rate in an acidic solution, there was several fold increase in the reaction speed by changing pH value of the solutions from 3 to 7, as can be seen in Figure 12. Therefore, the effect of pH value on the ozonation rate is very significant. Figure 12 also demonstrated that the Arrhenius equation can be employed to correlate the dependence of the rate constant on temperature. The influence of temperature on the rate of ozonation of benzene is most significant in strongly acidic solutions and least important in neutral solutions. The experimental results show that in acidic solutions with a pH value of 3, the reaction rate increased about 13 times with a temperature increase of 10°C. In neutral solutions, however, the rate increased no more than twice for the

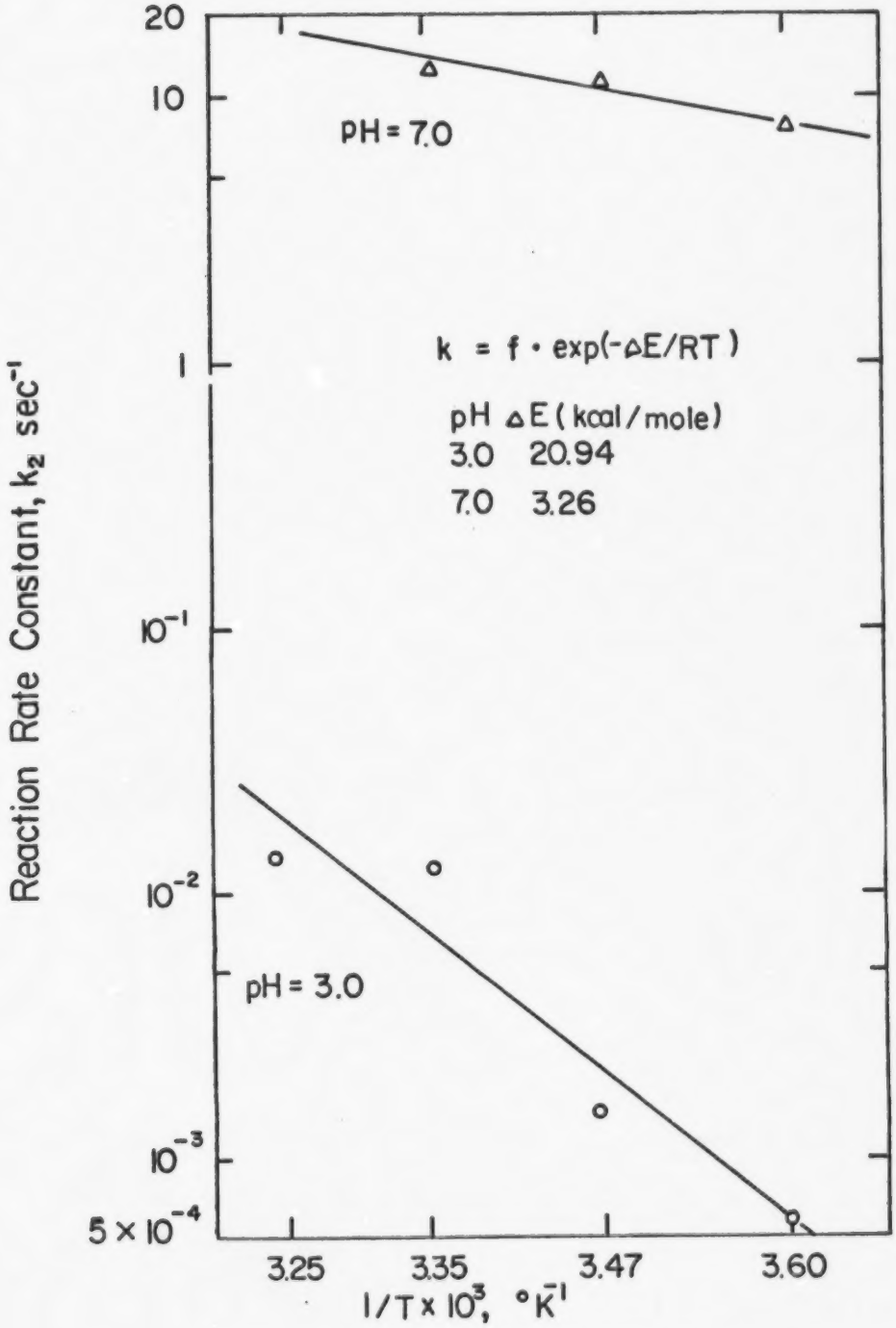


Figure 12. Average Ozonation Rate Constant For Benzene - Ozone Reactions

same temperature change of 10°C. The activation energies can be calculated from the slopes of the straight lines to be 20.94 and 3.26 k cal/g mole at pH values of 3 and 7, respectively. The significant change in activation energies at various pH values again suggests that the mechanisms of ozonation in the acidic solutions might be different from those in the neutral solutions.

An OV-17 glass column was used in the gas chromatograph to detect products of ozonation of benzene. Following the separation, the mass spectrometer was employed to obtain mass spectra of the individual species. Benzoquinone (p-quinone) was identified in all samples, but only hydroquinone (1.4-dihydroxy benzene) was detected in the neutral solution. Several spectra with molecular weights above 108 were detected but definite identification of these products has not been possible. The formation of phenol during ozonation of benzene in liquid phase was reported by Komissarov and Komissarova (11). However, no trace of phenol was found in the present work.

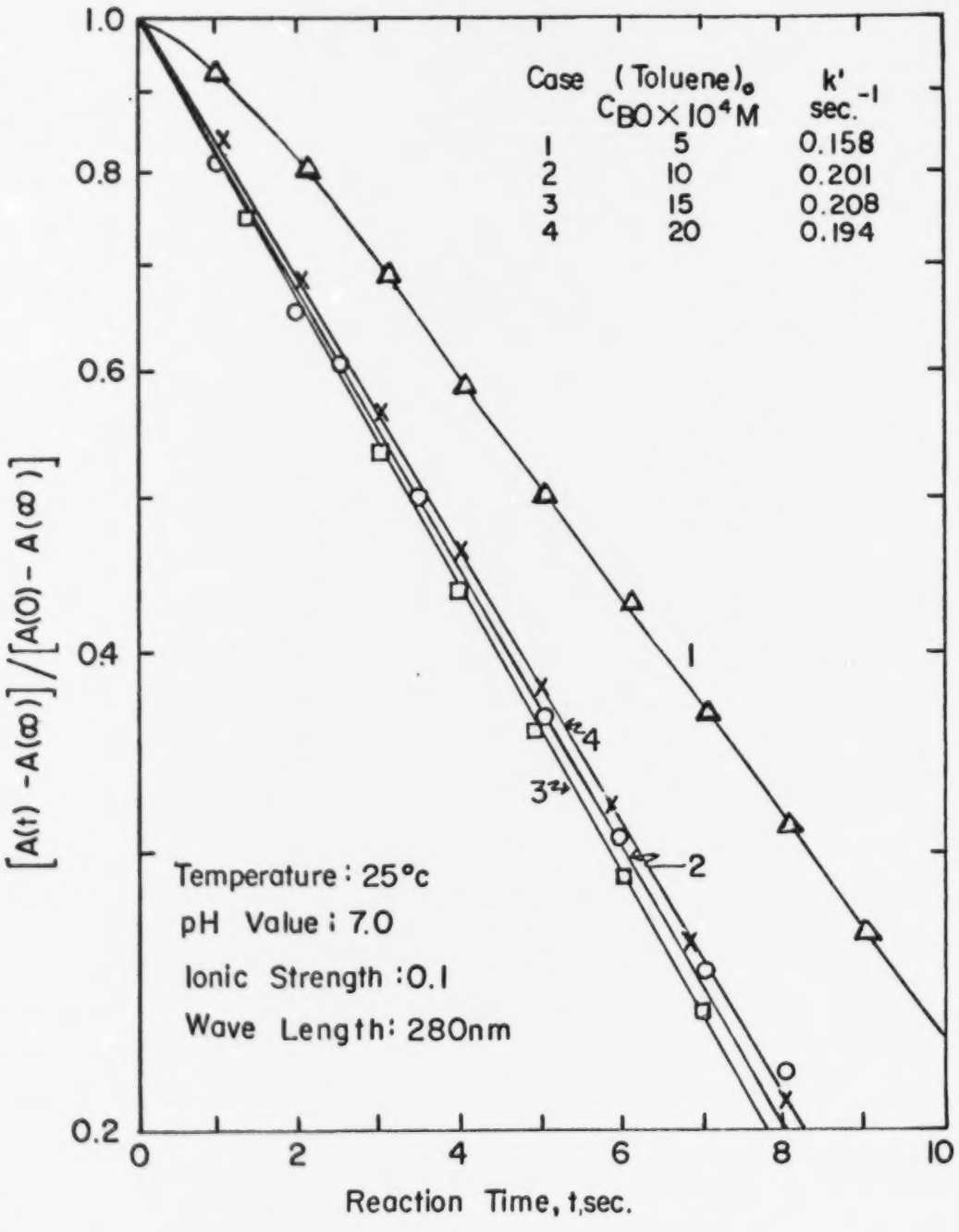
Several tests were conducted to observe color change during ozonation by continuous bubbling of ozone gas into aqueous solutions of benzene. In a strongly acidic solution with pH value of 3, no apparent change in color was observed. In distilled water and in neutral solutions containing benzene at an initial concentration of 0.01M, a light yellowish color appeared in the solutions following dispersion of ozone for one to two minutes. The color became darker as the bubbling of ozone continued, and the color disappeared after a total injection time of about 15 minutes. Absorbances of several standard reagents in aqueous solutions were measured at 270 nm. At a possible maximum concentration of 1×10^{-4}M for a product in the solutions, benzoquinone with yellowish color exhibited a small absorbance at 0.09. The absorbance of

hydroquinone which was colorless, on the other hand, was much larger at 0.175. In the kinetic experiments, the absorbances of the reaction products were found to be much higher in the neutral than in the acidic solutions. This also might explain the difference in product analyses indicated in the chromatograms. In the acidic solutions, very little hydroquinone was formed, and therefore, the absorbances of the product solutions were low and only benzoquinone was detected by the gas chromatograph. In the neutral solutions, the unstable benzoquinone might have reacted further to form hydroquinone as observed in the gas chromatogram, and therefore, significant absorbances resulted in the product solutions in the kinetic measurements.

A major pollutant in both air and water environments, benzene is considered stable in the vapor phase (16). Nevertheless, the product analyses and kinetic experiments conducted in this research suggest that benzene can be very reactive with ozone in aqueous solutions.

The kinetics of ozonation of toluene in aqueous solutions at 25°C was investigated to determine its reactivity in comparison with benzene. Absorbances during a reaction were measured at a wave length of 280 nm. The measured results indicated that the reaction products exhibited certain absorbances at this wave length though toluene has little absorbance in the solution. As shown in Figure 13, the experimental data obtained in the neutral solutions were best correlated by the pseudo-first order kinetics with respect to ozone concentration. The average first order rate constant is 0.19 sec^{-1} and the reactions were nearly independent of toluene concentration. These reactions were about 190 times faster than the decomposition reaction of ozone alone in neutral solutions. However, the rates were much slower than the ozonation rates of benzene at the corresponding conditions. In acidic solutions with a

Figure 13. Absorbance Curves For Toluene - Ozone Reactions



pH value of 3, the oxidation of toluene was found to be first order with respect to both concentrations of ozone and toluene. The apparent rate constant (first order) varied from 0.015 to 0.054 sec^{-1} as the initial concentration of toluene increased from 0.5×10^{-3} to 2×10^{-3}M, and the ozonation rate constant was calculated to be 25.6 1/mole-sec. as indicated in Table 4. The first order rate constants are slightly larger than 0.012 sec^{-1} obtained for benzene-ozone reactions in the acidic solutions with a pH value of 3 at 25°. Thus, the reactivity of toluene was slightly higher than that of benzene in acidic solutions though benzene was much more reactive with ozone in neutral solutions. It should be noted that the reactivity of toluene was reported to be higher than that of benzene (15,21,24,25). However, very little information is available in the literature concerning the rate of ozonation of toluene in the aqueous phase.

TABLE 4. REACTION ORDERS AND AVERAGE RATE CONSTANTS FOR TOLUENE-OZONE SYSTEMS

pH Value	Temperature, °C	Order with respect to Ozone(m)	Order with respect to Toluene(n)	Average Rate Constant, k_2
3.0	25.0	1.0	1.0	25.6
7.0	25.0	1.0	0	0.19

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